



Steady state and lean-rich cycling study of a three-way NO_x storage catalyst: Experiments

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ABSTRACT

The three-way NO_x storage catalyst (TWNSC) combines components from a conventional three-way catalyst (TWC) and NO_x storage and reduction (NSR) catalyst to improve NO_x emissions while exploiting the higher fuel economy of lean-burn gasoline vehicles. The performance of a commercial monolithic TWNSC was studied to understand the NO_x trapping and reduction performance over a range of conditions with emphasis on identifying conditions leading to optimal performance in terms of a standalone TWNSC or one coupled with a downstream selective catalytic reduction (SCR) device. Using H₂, CO, and C₃H₆ in various combinations, the impact of cycle timing (cycle time, rich duty fraction), reductant and O₂ feed concentrations, and feed temperature on NO_x conversion and product (N₂, NH₃, N₂O) selectivities was determined. Steady state experiments were conducted to assess catalyst activity and selectivity and to help interpret the phenomena observed during lean-rich switching. Cycling experiments reveal maxima in the NO_x conversion and ammonia-to-NO_x ratio (ANR) at distinct, intermediate cycle times. The existence of operating conditions giving these maxima depends on the reductant type, feed temperature, and O₂ feed concentration. For example, a large disparity in the lean/rich ratio (stoichiometric number) of the lean and rich feeds tends to lead to a NO_x conversion maximum. Where possible, the data trends are interpreted in terms of known performance features of the TWC and NSR catalysts. The study findings provide guidance for optimizing the TWNSC formulation and operation strategy.

1. Introduction

Consumer demand for gasoline-powered vehicles spanning passenger cars to light-duty trucks and SUVs has generally increased over the past 6 years [1]. At the same time, vehicle manufacturers must respond proactively to the increasingly stringent emission and fuel economy standards through the development of more efficient and cleaner emitting vehicles [2]. This requirement has led to increased interest in lean-burn engines, which are typically more fuel efficient than their more conventional stoichiometric counterparts. Dual mode engine operation affords a combination of lean-burn and stoichiometric combustion with transitions between each depending on driving conditions and power needs [3]. Stoichiometric gasoline vehicles are equipped with three-way catalysts (TWCs) to simultaneously eliminate CO, HCs, and NO_x. Fig. 1 shows the narrow air-to-fuel ratio window wherein TWCs are efficient in removing CO/hydrocarbons as well as NO_x. Outside of this window, conversion of reductants (CO, HCs) is difficult under rich conditions and conversion of NO_x is a challenge under lean conditions [4]. Fuel-lean operation results in excess (unreacted) O₂ in the exhaust gas. As a result, whereas the net oxidizing

exhaust enables the straightforward oxidation of partial combustion exhaust species CO and hydrocarbons (HCs), the catalytic reduction of NO_x (NO + NO₂) is more difficult [5,6]. Overall, TWCs are ineffective for the reduction of NO_x in diesel or lean-burn gasoline vehicle exhaust.

Considerable progress in reducing NO_x from diesel and lean burn gasoline vehicles has been made in recent years. Both the NO_x storage and reduction (NSR) and selective catalytic reduction (SCR) technologies have been developed and commercialized [7]. NSR is a cyclic process wherein NO_x is trapped during fuel-lean operating conditions and reduced to benign (N₂), less harmful (CO₂, N₂O), or more useful species (NH₃; see below) during a fuel-rich regeneration period [8]. Lean NO_x trap (LNT) catalysts require a combination of oxidation, reduction, and NO_x storage functionalities. Precious metals provide the first two functions, while oxides of alkaline earth metals provide the latter [9]. The basic LNT material contains BaO and Pt, with the former serving as the NO_x storage material, and the latter providing catalytic sites for NO oxidation and NO_x reduction [8,9]. Many previous studies have explored the NSR mechanism through which NO_x is stored on the catalyst surface, i.e., the nitrite and nitrate routes [10]. Epling et al. provided evidence for two types of sites for NO_x adsorption, namely

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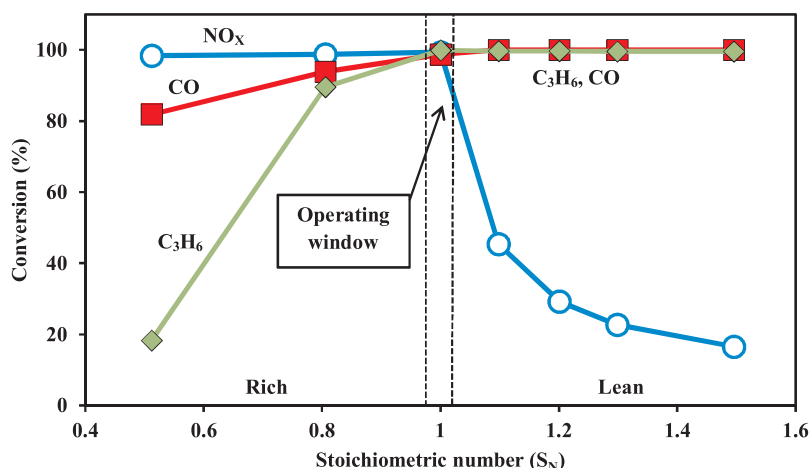


Fig. 1. TWC Performance Curve. Operating a TWC to the left or right of the operating window leads to significant performance loss. (The details of these data will be explained in the Results and Discussion section).

sites close to Pt that undergo the nitrite pathway, with subsequent oxidation to nitrates, and sites farther away where nitrates form via disproportionation [11]. Kumar et al. showed that the two populations of sites are a manifestation of stored NO_x diffusion limitations [12].

During the subsequent rich phase or regeneration step the stored NO_x is released and reduced, leading to the mixture of the aforementioned N-containing products: N₂, N₂O and NH₃. Various studies detail the interaction between the precious metal and stored nitrates or nitrites on the surface, namely the reverse spillover process, in which “proximal” nitrates and nitrites decompose, leading to NO that is catalytically converted to N₂ on the Pt [9,13]. In addition to this chemistry, at high temperatures H₂O can react with CO or HC to form H₂, which results in higher selectivity to NH₃ [9,14,15]. Furthermore, the presence of H₂ on the Pt surface during this phase leads to H₂ dissociation that can reduce nearby NO species through a “forward spillover” process [16].

In contrast to NSR, selective catalytic reduction (SCR) requires the deliberate injection of NH₃ into or formation of NH₃ in the exhaust system; the latter is typically accomplished by the thermal conversion of aqueous urea [17]. Exhaust NO_x combines with NH₃ and O₂ to form N₂ and H₂O, mainly over zeolite catalysts via three main pathways: standard SCR (NH₃ + NO + O₂); NO₂ SCR (NH₃ + NO₂); and fast SCR (NH₃ + NO + NO₂).

In recent years there has been increased interest in combining NSR and SCR technologies [18,19]. One such application involves the use of a LNT to generate NH₃ for a downstream SCR catalyst [19]. The main advantage of this approach is that an external source of NH₃ is not needed, while the main disadvantage is that periodic operation is required. One of the key metrics used to understand and to optimize SCR behavior is the ratio of NH₃ produced to NO_x slipped from the upstream NSR catalyst (Ammonia-to-NO_x ratio, ANR) [17,19–21].

In order to remove NO_x from the exhaust gas and still operate the engine with a higher air to fuel ratio than the TWC, the concept of combining the TWC with NO_x storage functionality was first proposed by Ikeda et al. as the three-way NO_x storage and reduction catalyst (TWNSC) [22]. While the TWNSC is generally applied to lean gasoline engine emission control, it serves a similar role as that of the sequence of the diesel oxidation catalyst (DOC) + LNT encountered in diesel emission control. Unlike the DOC + LNT, which operates with sustained lean-rich cycling, the TWNSC serves to trap NO_x during the lean acceleration modes and to regenerate during coast/deceleration modes of engine operation. The challenge is to achieve a balance between the two catalyst functionalities while saving space and cost. As one might expect, there are many parameters involved in achieving or even optimizing this balance, such as the total cycle time, the fraction of the

cycle that the engine is in regeneration mode, etc. [9]. Performance metrics would certainly include conversion of NO_x, CO, and HC, and the selectivity to N₂, N₂O, and NH₃.

Recent experimental studies provide important insight about the modified TWC. The study by Theis et al. of a TWC + SCR system showed that all of the NH₃ was produced during the rich phase, implying the importance of finding the right balance between cycle time and conversion or selectivity [23]. DiGiulio et al. characterized different TWCs and their comparative abilities in generating NH₃ for use in a downstream SCR, a system referred to as passive-ammonia SCR [24]. In their work, four catalyst systems were examined, one of which was an NSR catalyst operating as a TWC. The study showed that the periodic operation expectedly generates NH₃ and the addition of a NO_x storage component to a TWC lowers the required duration of the rich period while increasing the fuel economy. One of the main drawbacks is the decreased CO conversion at low catalyst temperatures; an effect that must be addressed in future studies [24].

The objective of this study is to systematically evaluate the performance of a commercial TWNSC under a range of cycling protocols. Specific attention is placed on the impacts of operating parameters on conversion and product distribution. The data are interpreted in terms of the anticipated application, be it a standalone unit intended to maximize the NO_x conversion and N₂ selectivity or a TWNSC + SCR tandem unit in which the intent is to shift up to half of the NO_x conversion to the downstream SCR. Conditions are identified that lead to best performance for each application. Where possible, the performance trends are interpreted from the standpoint of known TWC and NSR features. It is important to note that the TWNSC is meant to operate once the vehicle has warmed up to allow sufficient activity of the emission catalyst. In principle, the TWNSC could be modified to enable low temperature HC and NO_x trapping. However, this effect was not a focus of the current study and thus low temperature data are not discussed.

2. Experimental

The commercial TWNSC used in this work was received from Fiat Chrysler Automobiles LLC. (FCA). The commercially supplied catalyst is a mixed catalyst containing precious group metals (PGM) comprising a mixture of TWC and LNT components such as barium oxide (for NO_x storage), ceria (for oxygen storage), and alumina (binder). Table 1 provides the ICP-measured mass percentages of the oxide components (Ba, Ce, Al, La, and Zr). The precious group metal mass percentage was ~1.2 wt.% in a Pd:Pt:Rh ratio of 73:26:1. Samples were cut from a monolith “brick” to ~1 cm in diameter and 1.8 cm long. CO

Table 1

Mass percentages of the washcoat oxide components measured by ICP.

Element	Al	Ba	Ce	La	Pt + Pd + Rh	Zr
wt. %	19.30%	4.70%	9.96%	1.22%	1.16%	8.92%

chemisorption using a Micromeritics apparatus gave a PGM metal dispersion of ~40% for a fresh sample, before degreening. Because the ratio of Pd:Pt:Rh in the sample is known, an average value for the stoichiometry factor was determined in order to calculate the dispersion, which in this case is 1.0. One sample was used for all the catalyst performance experiments conducted in this work, which was degreened at 700 °C for 4 h in 10% H₂O and 10% CO₂ with a balance of Ar. The sample was then wrapped in ceramic paper and placed in a horizontal-flow quartz tube reactor. The total flow rate was kept constant at 3000 sccm (standard cm³/min), which corresponds to a gas hourly space velocity at standard conditions of 99,000 h⁻¹. Inlet and outlet lines were maintained at 180 °C to prevent condensation. Effluent concentrations were measured using a Thermo Scientific FT-IR (6700 Nicolet). Three type-K thermocouples (Omega Engineering) were used to monitor the temperatures within the system. One was placed 0.5 cm upstream of the catalyst (T_{feed}); the second was placed in the radial and axial center of the catalyst (T_{cat}); and the third was placed 0.5 cm downstream (T_{out}). T_{feed} and T_{cat} were used as the reference temperatures for the experiments in this work.

For the steady state experiments, the catalyst was first pretreated with 5% O₂, 10% CO₂, and 7% H₂O at 500 °C for 20 min. After the pretreatment, the reactor was purged for 10 min with Ar, and was cooled to the desired feed temperature during which time a steady flow of feed gases was established through the bypass. Once the reactor temperature was stable, the flow was switched from the bypass to the reactor, and the effluent concentrations were monitored until steady concentrations (± 2%) were obtained for at least 10 min. The desired feed temperature was achieved by adjustment of the furnace temperature.

NO_x storage experiments were conducted in the same quartz tube reactor. First, the catalyst was pretreated in a feed of 2% H₂ at the feed temperature for 30 min, after which the catalyst was purged under argon for 10 min. During adsorption, a feed containing 500 ppm NO and 5% O₂ was introduced to the catalyst until the output concentration reached steady state (i.e. saturation). The NO/O₂ mixture was then turned off and the catalyst was held at the adsorption temperature until the outlet concentration of NO_x reached zero, eliminating any weakly adsorbed NO_x from the surface. Then the catalyst underwent a temperature-programmed desorption under Ar at a rate of 10 °C/min up to 600 °C. This procedure was repeated for a variety of feed temperatures ranging from 130 °C to 415 °C.

In this work, the stoichiometric number is used to characterize the feed composition:

$$S_N = \frac{2C_{O_2} + C_{NO}}{C_{CO} + C_{H_2} + 9C_{C_3H_6}} \quad (1)$$

S_N measures the deviation of the catalyst environment from a stoichiometric neutral feed (S_N = 1). Unless otherwise specified, the feed composition consisted of 1% CO, 3300 ppm H₂, 500 ppm NO, 10% CO₂, 7% H₂O, and a variable concentration of O₂ to achieve a certain S_N. When propylene was used its concentration was 1000 ppm. The balance of all mixtures was Ar in order to maintain a constant total feed flow-rate and space velocity.

For the cycling experiments, the same pretreatment was used, followed by a 10 min Ar purge. Instead of establishing a steady flow through the bypass, a steady cycling profile through the bypass was obtained. A pseudo steady state was defined by an unchanging effluent temporal profile for at least 5 cycles. Once the feed was established and the reactor temperature stabilized, the flow was switched to the reactor

tube and effluent concentrations were measured until 10 repeatable cycles were obtained. The feed system enables precise control of the rich and lean feeds to as short as a 1 s duration. In this study, typical total cycle times, τ_T, were in the range of 20–60 s with rich duty fractions, d_r, between 0.05 and 0.7, with the following definitions:

$$\tau_T = \tau_r + \tau_l \quad (2a)$$

$$d_i = \frac{\tau_i}{\tau_T} \quad i = r, l \quad (2b)$$

Details of more complex cycling experiments are described later in the Results and Discussion section of this work.

Several performance metrics were defined and calculated, including reactant conversion, selectivity, and yield. The cyclic values were time integrated over at least 5 cycles, yielding a cycle-averaged value. The cycle-averaged NO_x conversion is defined as:

$$X_{NO_x} = \frac{\int C_{NO_{x,in}} - \int C_{NO_{x,out}}}{\int C_{NO_{x,in}}} \quad (3)$$

with the NO_x concentration the sum of NO and NO₂. The cycle-averaged CO conversion is similarly defined as:

$$X_{CO} = \frac{\int C_{CO,in} - \int C_{CO,out}}{\int C_{CO,in}} \quad (4)$$

A similar equation was used to calculate the conversion of C₃H₆. The corresponding steady state quantities were obtained using standard definitions. The cycle-averaged selectivity of the N-containing product is given by:

$$S_{N_{species}} = \frac{\alpha \int C_{N-species,out}}{\int C_{NO_{x,reacted}}} \quad (5)$$

where α represents the molar coefficient of the species (α = 1 for NO, NO₂ and NH₃; α = 2 for N₂O). The N₂ selectivity was calculated by difference of the other species selectivities. The NH₃ yield is defined by:

$$Y_{NH_3} = \frac{\int C_{NH_3,out}}{\int C_{NO_{x,in}}} \quad (6)$$

In addition to conversion and selectivity, the cycle-averaged temperature was determined using a similar time-integrated method. Finally, the ratio of ammonia produced to NO_x slip (ANR) is defined by:

$$ANR = \frac{\int C_{NH_3,out}}{\int C_{NO_{x,out}}} \quad (7)$$

The lean NO_x storage efficiency, η_l, is the fraction of NO_x stored during the lean phase of duration τ_l:

$$\eta_l = \frac{C_{NO_{x,in}} * \tau_l - \int C_{NO_{x,out}} d\tau_l}{C_{NO_{x,in}} * \tau_l} * 100 \quad (8)$$

3. Results and discussion

3.1. Steady state catalyst performance

A series of steady state experiments was used to characterize the TWNSC activity and performance over a range of feed temperatures and compositions spanning lean to rich as described above in the Experimental section.

The steady state NH₃, CO, NO_x, and N₂O effluent concentrations under various lean or rich feed conditions at a fixed feed temperature of 270 °C are shown in Fig. 2. The figure also reports the mid-core temperature rise, measured as the difference between mid-catalyst temperature and feed temperature, T_{cat} – T_{feed}. The inset shows an expanded view of the 0.85 < S_N < 1.15 range, and also includes concentrations of individual NO_x components NO and NO₂. The stoichiometric condition (S_N = 1) is the demarcation between the lean and

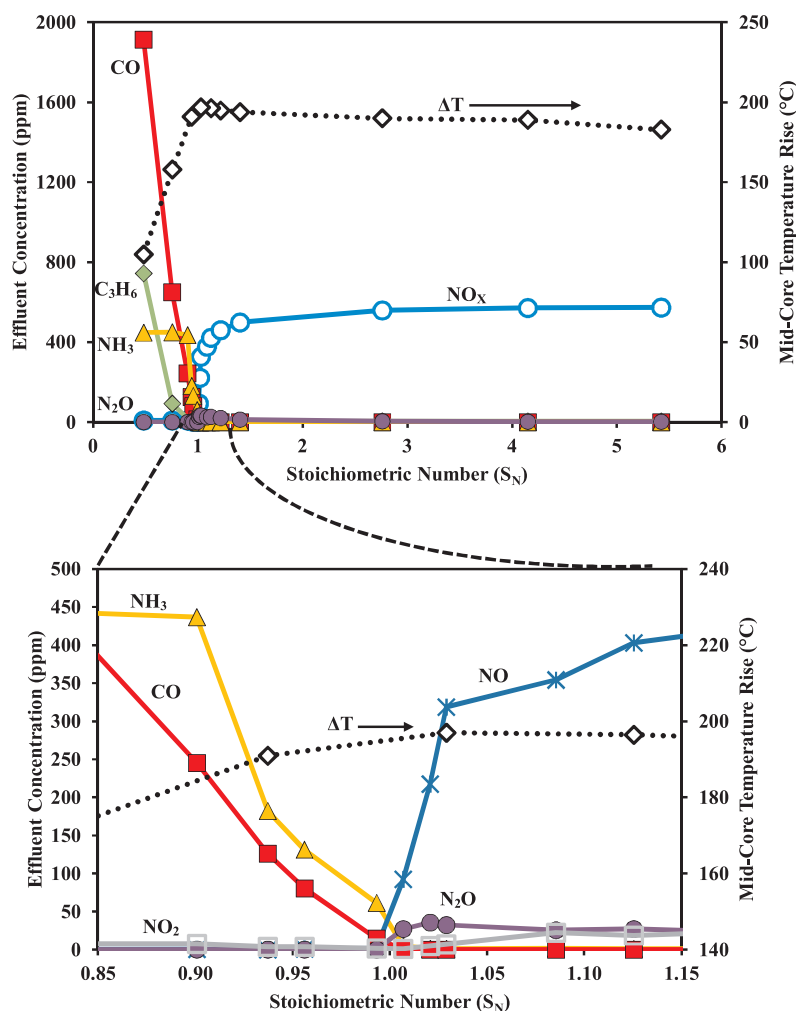


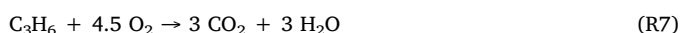
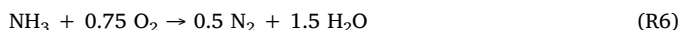
Fig. 2. Steady state effluent concentrations of NH_3 , CO , C_3H_6 , NO_x (incl. NO and NO_2), and N_2O (ppm) and catalyst temperature rise ($^{\circ}\text{C}$) vs. stoichiometric number (S_N) varying from lean to rich. $T_{\text{feed}} = 270^{\circ}\text{C}$. Inlet concentrations of $\text{CO} = 1\%$, $\text{NO} = 500$ ppm, $\text{C}_3\text{H}_6 = 1000$ ppm, $\text{H}_2 = 3300$ ppm, $\text{H}_2\text{O} = 7\%$, $\text{CO}_2 = 10\%$, varied O_2 .

rich feeds. At $S_N = 1$ the reacting species concentrations approach zero, as expected.

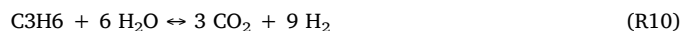
To the left of the neutral feed (Fig. 2) is the rich regime ($S_N < 1$). As S_N decreases from unity, the NH_3 concentration increases, the CO and C_3H_6 concentrations increase (conversions decrease), and the NO_x concentration approaches zero (complete NO_x conversion). In an O_2 deficient condition the NO_x is reduced to either N_2 or NH_3 with negligible production of N_2O . The increasing levels of CO and C_3H_6 with decreasing S_N result in a shift to NH_3 as the main N-containing product. Global chemical reactions that occur under rich conditions include NO reduction by the reductants:



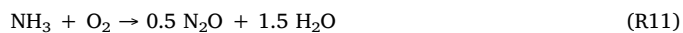
Under rich conditions both complete and partial oxidation reactions may occur:



Additionally, reactions involving H_2O as a reactant include water gas shift and reforming:



To the right of the stoichiometric condition is the lean regime ($S_N > 1$). The global reactions occurring under the stoichiometric excess are expectedly oxidation of the various species, including the previously identified total oxidation reactions (R4, R5, R6, and R7). Other oxidation reactions that can occur, include NH_3 oxidation to N_2O and NO :



and NO oxidation to NO_2 :



The distribution of nitrogen oxides depends on the temperature and O_2 concentration, among other factors [21]. For this set of conditions, NO oxidation to NO_2 in the range of $1.0 < S_N < 1.5$ is minimal. The low NO_2 concentration is in part a result of its reactivity as an oxidant. Reaction may also occur between NH_3 and NO especially near the

stoichiometric point. As S_N increases from unity, very little NH_3 , CO , and C_3H_6 are detected due to their respective oxidations, while a low but nonzero N_2O concentration is observed, as well as a shallow N_2O maximum at $S_N \sim 1.02$, before decreasing towards zero for $S_N > 1.5$. NO_x concentrations increase sharply with increasing S_N , approaching the feed value of 500 ppm by $S_N \sim 2$. The inset reveals that in a slight excess of O_2 ($S_N \sim 1.01$) all of the reductants are oxidized, as expected. The negligible but non-zero N_2O level for higher S_N is attributed to the presence of NO and O_2 in the gas phase [25]. Under these slightly lean steady state conditions, the precious metal sites are occupied by an admixture of O , NO and N species. N_2O can form through the following reaction [26]:

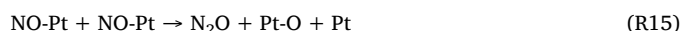


The N_2O maximum reflects adsorbed oxygen inhibition of NO sorption and reaction. At sufficiently large S_N the inhibition is sufficient so as to prevent N_2O formation.

The catalyst temperature rise reaches a maximum of $\sim 200^\circ\text{C}$ near $S_N = 1$. The maximum is attributed to the complete conversion of the reductants that results in the highest exotherm. With the temperature rise as a measure of the aggregate conversions of the reactants, it follows that full conversion of all species leads to the highest temperature rise. The slight decrease with increasing S_N beyond 1 is due to the non-adiabatic nature of the reactor. With increasing S_N , the oxidation reactions occur at higher rates, and thus became more localized towards the upstream portion of the catalyst. As the reactions occur more in the upstream portion, some heat loss can occur downstream.

Fig. 3 shows the conversions and selectivities of the reacting and product species over a range of feed temperatures for a slightly lean, almost stoichiometric feed ($S_N = 1.01$). The NO_x , C_3H_6 , and CO conversions are shown in Fig. 3a, while the selectivities to N_2O , NH_3 , and N_2 (by difference) are shown in Fig. 3b. As the feed temperature

increases from ~ 150 to 200°C , the CO and C_3H_6 conversions sharply increase to 100%. In contrast, the NO_x conversion reaches a 60% maximum at $\sim 275^\circ\text{C}$ before decreasing to $\sim 35\%$ at 500°C . The NO_x conversion maximum is attributed to the competing effects of adsorption, desorption, and reaction. At low temperature, CO and NO are not converted due to self-inhibition [27]. As the temperature increases, surface reactions commence, including CO and C_3H_6 oxidation, as well as NO_x conversion to N_2O and N_2 . The abrupt increase in conversion of CO and C_3H_6 is indicative of a reduction in CO coverage due to CO desorption, freeing up sites for oxidation. At sufficiently high temperature an increased rate of NO desorption leads to a decline in NO_x conversion. The decreasing N_2O selectivity (Fig. 3b) is due in part to a declining availability of NO due to the increasing NO desorption rate. That N_2O is highest at low temperature is a result of the lower rate of N-O bond scission, making NO available to react through N-NO (R14) or NO-NO coupling [28]:



N_2O formation sharply decreases at higher temperatures due to the increased selectivity to N_2 , a result of an increased rate of N-O bond scission at higher temperatures, minimizing the presence of NO available for N-NO coupling, and yielding N-N coupling instead.

Finally, NH_3 formation is favored under rich conditions, which for $S_N = 1.01$ (slightly lean) is negligible [29]. The observed small but nonzero NH_3 selectivity at 150°C is attributed to low temperature formation of NH_3 via H_2 , even though the feed is slightly lean. It was previously shown that H_2 reacts readily with NO to form a mixture of N_2O , N_2 , and NH_3 on Pt at low temperature and anaerobic conditions [30]. In the presence of a slight excess of O_2 there is competition between O_2 and NO to oxidize H_2 , leading to the negligible but nonzero formation of NH_3 . That is, H_2 oxidation by O_2 is apparently not fast enough at low temperatures, allowing for NO reduction by H_2 .

3.2. NO_x storage evaluation

In order to evaluate the ability for the TWNSC to store NO_x during the lean phase, a series of experiments was conducted at a variety of feed temperatures in which a feed of 500 ppm NO and 2% O_2 was fed over the catalyst. The results of this experiment are shown in Fig. 4, which plots the average amount of total NO_x adsorbed and desorbed vs feed temperature. Because the adsorption experiment was conducted until the catalyst reached saturation of NO_x , the values in Fig. 4 represent the total NO_x storage capacity of the TWNSC at the given feed temperature. The error between the calculated amount of stored NO_x is less than 10% in most cases, so the mass balance between the two measurements is closed. Note that the adsorption capacity of the

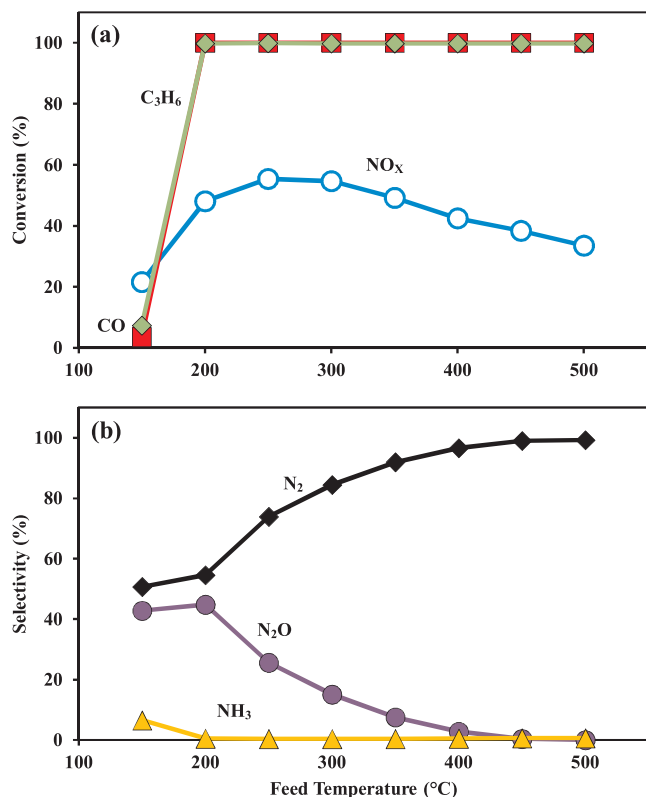


Fig. 3. a, b. (a) Steady state CO , NO_x , and C_3H_6 conversion vs. feed temperature. (b) Steady state N_2 , N_2O and NH_3 selectivity vs. feed temperature. $S_N = 1.01$. Inlet concentrations of $\text{CO} = 1\%$, $\text{NO} = 500$ ppm, $\text{C}_3\text{H}_6 = 1000$ ppm, $\text{H}_2 = 3300$ ppm, $\text{H}_2\text{O} = 7\%$, $\text{CO}_2 = 10\%$, $\text{O}_2 = 1.08\%$.

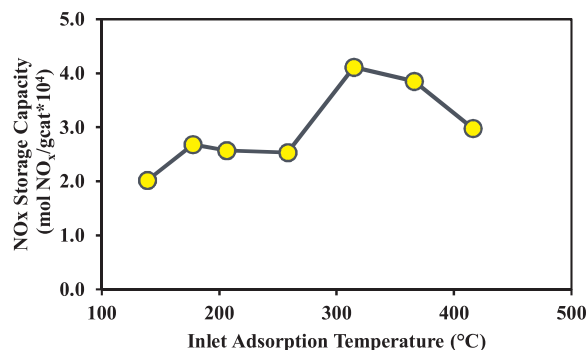


Fig. 4. Lean NO_x storage capacity vs. inlet adsorption temperature. Values shown represent the total storage capacity (saturation point) of the TWNSC sample as an average of the adsorption and desorption values calculated for each experiment. Catalyst was pre-reduced at the feed temperature using 2% H_2/Ar . During adsorption, feed consisted of 500 ppm NO in 5% O_2 , and during desorption the feed contained only Ar .

TWNSC is bimodal in that there are two local adsorption maxima, consistent with earlier studies of lean NO_x trap adsorption behavior [33]. This type of behavior suggests storage on two types of sites, namely BaO and either alumina and/or ceria. Note also that H₂O is not present in these experiments, which leads to a significant increase in NO_x storage performance when compared to cycling data that contains the full simulated exhaust feed.

3.3. Lean-rich cycling experiments

For application in lean combustion exhaust, the transient and cyclic performance of the TWNSC is critical since NO_x trapping during lean periods and reduction during rich periods must be effective. With cyclic operation, there are several additional operating parameters which present both a challenge and opportunity for optimizing TWNSC performance. In the next several sections the impacts of these parameters on catalyst performance are evaluated. The operating parameters that are varied include the rich time (τ_r), lean time (τ_l), and total cycle time (Eqs. (2a) and 2b). It is convenient to define lean and rich stoichiometric numbers ($S_{N,l}$; $S_{N,r}$), thereby defining a cycle-averaged stoichiometric number ($S_{N,avg} = (1 - d_r)S_{N,l} + d_r S_{N,r}$), which will influence performance. To achieve a prescribed $S_{N,r}$ the rich phase composition is adjusted through the reductant and O₂ concentrations. Finally, there are additional parameters including the feed temperature (T_{feed}) and flowrate.

3.3.1. Baseline cyclic performance

Typical transient cycling data are shown in Fig. 5 for a feed when the temperature (T_{feed}) is fixed at 270 °C and lean and rich times are fixed at 25 s ($\tau_T = 50$ s, $d_r = \tau_r/\tau_T = 0.5$). The feed gas contains 500 ppm NO, 1% CO, 3300 ppm H₂, 7% H₂O, and 10% CO₂ with O₂ switched between 5% during the lean and 0.3% during the rich. These concentrations give $S_{N,l} = 7.55$ and $S_{N,r} = 0.45$ and a cycle-averaged value of $S_{N,avg} = 4.03$, which is a net-lean feed.

During the lean phase of the cycle, ~80% of the feed NO is trapped on the catalyst based on an analysis of the transient NO_x data shown in Fig. 5a. There is a short period of duration of ~3 s during which no NO_x is observed. This is followed by breakthrough and a monotonic increase in NO_x concentration up to the start of the rich phase, indicating storage of NO_x throughout the lean cycle. These trends are similar to those reported for the typical storage phase of a lean NO_x trap [8]. During the lean phase, NH₃ and CO concentrations drop to zero with the NH₃ concentration tail more protracted than CO. The NH₃ tail is due in part to the propensity of NH₃ to adhere to surfaces, delaying its decrease to zero [31]. This effect was proven with a blank tube experiment (data not shown here). It is also noted that with the large excess of O₂ during the lean phase, NO storage generally occurs through its oxidation to NO₂ which stores on trapping sites. The presence of NO₂ and lack of N₂O during the lean cycle confirms this. Fig. 5b shows the transient profile of the NO_x components, NO and NO₂. At the start of the lean phase, there is a slight decrease in NO₂ concentration, due to lean storage of some residual NO₂ present at the end of the rich phase, followed by a minimum before its breakthrough. The NO₂ breakthrough is delayed relative to that of NO. We attribute this to the balance between the rates of NO oxidation to NO₂, the rate of adsorption, and the sustained feed of NO [31,32].

NO₂ is more readily adsorbed than NO, as has also been shown for lean NO_x traps [9]. Once NO breakthrough is observed, NO₂, formed through NO oxidation, continues to adsorb. As the storage sites become saturated, NO oxidation continues and NO₂ breakthrough occurs throughout the remainder of the lean cycle. During this period oxygen is also stored on the catalyst, both on the precious metal crystallites and on/in the ceria phase.

During the rich phase of the cycle the formation of NH₃, N₂O, and N₂ involve complex chemistry that depends on many variables including the local catalyst temperature, the relative supply of the various

reacting species, and oxygen coverage on the precious metal crystallites, among other factors [33]. The transient data have three notable features.

First, just after the switch to the rich phase there is a brief increase in the NO_x concentration, akin to the “NO_x puff” encountered during regeneration of stored NO_x on the LNT catalyst [34]. In NSR studies the NO_x puff is attributed to the difference between the rate of stored nitrite/nitrate decomposition leading to NO_x release and the rate of NO_x reduction [10,34]. As regeneration proceeds, less NO_x is released, allowing the reduction rate to exceed the release rate leading to the eventual decrease in NO_x concentration. A vanishing NO_x concentration means that its reduction rate is high relative to the release rate. In some NSR studies the NO_x concentration during the puff may exceed the feed NO_x concentration value as the accumulated stored NO_x desorbs rapidly and with its sustained feed leads to this short-lived additive effect [34].

Second, at about the same time that the NO_x concentration approaches zero, both NH₃ and CO breakthrough are observed. The NH₃ originates from the reduction of both feed NO and NO_x stored during the previous lean phase. NH₃ formation behaves as expected during the rich phase, consistent with the steady state and other experiments [35]. The delay in the breakthrough of NH₃ and CO is attributed to their reactions with oxygen and NO_x stored downstream on ceria and barium components [33]. While there is O₂ in the rich phase inlet gas (0.3%), it is mostly consumed in the net rich environment ($S_{N,r} = 0.45$). Oxygen is stored on the catalyst, most notably on the ceria phase, and is consumed by the feed reductant and the formed NH₃. Production of NH₃ via H₂ or CO takes place once the Pt surface is fully reduced and less O and NO is available [33,36]. Eventually the surface O is consumed through oxidation of the incoming reductants, and at that point reductant breakthrough is observed. During this period there is a small increase in NO₂, indicating equilibrium between NO on the surface being reduced or decomposing to form N and O adatoms that could partially form NO₂. This process evolves spatially; consumption of stored oxygen occurs upstream and moves through the monolith. NH₃ is generated in the oxygen-deficient zone and moves closely behind the CO and H₂ reductant front, and, like H₂, NH₃ will readily react with stored oxygen (on the ceria phase) and stored NO_x (on the barium and ceria phases) [33].

The third feature is the small but detectable formation of N₂O evident early in the rich phase, followed by its decrease to zero. N₂O is formed due to NO bond scission, generating N adatoms which react with the NO released at the commencement of the regeneration (R14 and R15). Another route is from the reaction between NH₃ formed upstream and NO_x stored downstream [33]. These data do not show evidence for a second peak which has been reported during NSR studies (e.g., [36]).

The temperature profile for the previously discussed lean and rich cycles is shown in Fig. 5c. As expected, during the lean phase in which combustion of hydrocarbons occurs, there is an increase in the catalyst temperature, peaking at 130 °C relative to the feed temperature. This value corresponds to a peak absolute catalyst temperature of 405 °C. After transitioning to the rich phase, the temperature starts to drop since the large exotherms from combustion are not present. Using this data, a cycle-averaged feed temperature and temperature rise can be calculated, as shown in the figure.

3.3.2. Impact of rich injection intensity

A series of experiments was conducted in which the total amount (volume or moles) of reductant was fixed, while the time over which the reductant was injected was varied. Of interest is whether the reductant injection strategy provides an opportunity to optimize the NO_x conversion in the case of the standalone TWNSC or the NO_x conversion and NH₃ selectivity for the TWNSC + SCR system. In a previous LNT study, Kabin et al. [37] varied the rich phase intensity using C₃H₆ as reductant. More recently Shakya et al. [38] examined the effect of H₂

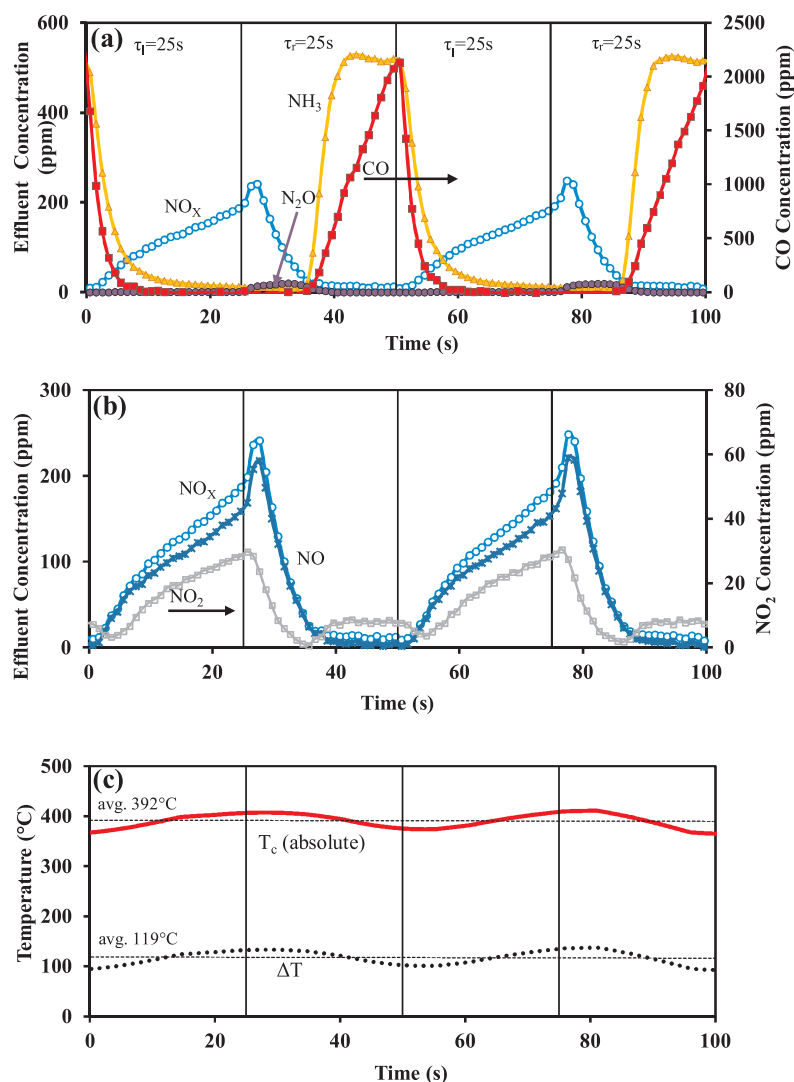


Fig. 5. a,b,c. Transient data for lean-rich cycling of TWNSC. (a) Effluent concentration of NO_x, NH₃, CO, N₂O. (b) NO_x profile as components NO and NO₂. (c) Catalyst temperature (T_c , avg = 392 °C) and catalyst temperature rise (ΔT = 119 °C). T_{feed} = 270 °C. Lean inlet concentrations ($S_{N,l}$ = 7.55): 500 ppm NO, 1% CO, 3300 ppm H₂, 7% H₂O, 10% CO₂, 5% O₂. Rich inlet concentrations ($S_{N,r}$ = 0.45): 500 ppm NO, 1% CO, 3300 ppm H₂, 7% H₂O, 10% CO₂, 0.3% O₂.

reductant intensity during NO_x storage and reduction on a Pt/BaO NSR monolith catalyst.

Fig. 6 shows the cycle-averaged results in which the rich duty percentage ($100 \cdot d_r$) varies over a 5–70% range for five different feeds during a cycle having a fixed lean duration of $\tau_l = 40$ s. The rich time (τ_r) and rich reductant feed volume fraction (C_r , %v.) was adjusted to maintain a fixed volume of reductant ($V_r = V_{CO+H_2} = \text{constant}$; CO/H₂ = 3) according to

$$C_r = \frac{100 V_r}{d_r \tau_r Q_T} \quad (9)$$

where V_r is the volume of reductant (CO + H₂) (in standard cm³, or scc), d_r is the duty fraction of the rich phase, τ_r is the total cycle time (s), and Q_T is the standard volumetric flow rate of the feed (scc/s); V_r and Q_T are evaluated at standard conditions. Table 2 summarizes the feed parameters for each of the five feeds. For four of the Feeds (I, II, III, IV) the fixed reductant amount is 20 scc while for Feed V the fixed amount is 10 scc. The fixed amount (10 or 20 scc) was varied to access a wider range of rich duty fraction values (for fixed C_r). The volumetric concentration of O₂ in the rich feed was fixed at three different levels, 0%, 0.27%, and 0.53%. Feeds IV and V represent the case in which the O₂ is varied tightly around the stoichiometric point; i.e. 0.8% O₂ during the lean phase ($S_{N,l} = 1.24$) and 0.53% during the rich phase. The feed

temperature was fixed at 270 °C for four of the five Feeds (I, II, IV, V) and at 470 °C for Feed III.

Fig. 6a and b shows the rich phase stoichiometric number ($S_{N,r}$) and cycle-averaged NO_x conversion (X_{NO_x}) as a function of rich duty percentage, $100d_r = 100\tau_r/\tau_T$. Fig. 6c and d shows the effect of the rich duty percentage on the cycle-averaged CO conversion (X_{CO}) and NH₃ selectivity (S_{NH_3}), respectively. Fig. 6e similarly shows the NH₃ yield. Each point in the figures represents one cycling experiment.

Examination of Fig. 6 reveals several notable trends. First, the NO_x conversion (Fig. 6b) for each case generally increases with d_r up to a value in which a neutral stoichiometric mixture is achieved, i.e. $d_r(S_{N,r} = 1)$. Those values are provided in Table 2 for each feed. For $d_r > d_r(S_{N,r} = 1)$ the NO_x conversion decreases as the gas phase becomes net lean. This trend reflects that a rich phase that is both more prolonged and of a lower reductant concentration is more effective than a shorter, more intense pulse, as long as the feed does not become lean ($S_N > 1$). For example, for Feed II, X_{NO_x} [$d_r = 0.20$; $\tau_T = 50$ s, $y_{r,CO} + y_{r,H_2} = 0.04$] = 51%, while X_{NO_x} [$d_r = 0.60$; $\tau_T = 100$ s; $y_{r,CO} + y_{r,H_2} = 0.0067$] = 67%, with $y_{r,CO} = 3y_{r,H_2}$.

Fig. 6b shows that for fixed d_r , the NO_x conversion decreases with increasing rich phase O₂ concentration (increasing $S_{N,r}$) and increasing feed temperature ($T_f = 270$ –470 °C). The former trend underscores that increased reductant enhances NO_x conversion. The latter trend reflects

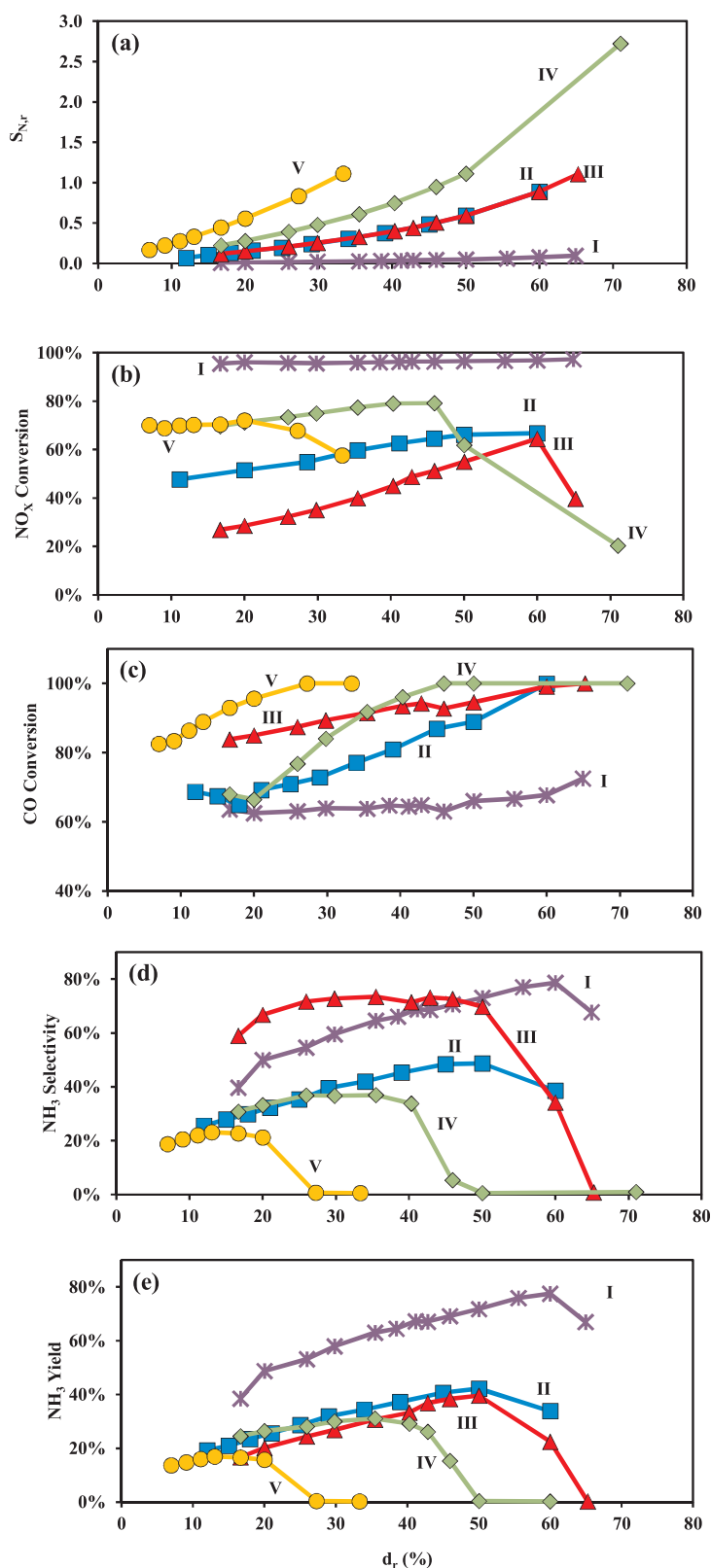


Fig. 6. a–e. (a) $S_{N,r}$ as a function of each duty fraction tested for experiments I–V. (b,c,d,e) Cycle averaged NO_x and CO conversion, NH_3 yield and selectivity, respectively. $\tau_l = 40$ s, τ_r varied based on d_r value. Lean inlet concentrations ($S_N = 1.24$): 500 ppm NO, 1% CO, 3300 ppm H_2 , 7% H_2O , 10% CO_2 , 0.8% O_2 . Rich inlet concentrations: 500 ppm NO, 7% H_2O , 10% CO_2 , var. O_2 , varied CO/ H_2 concentration (total amount of reductant fixed at 10 or 20cc, $V_{\text{CO}}/V_{\text{H}_2} = 3$).

the detrimental impact on NO_x storage capacity at high temperature. In contrast to NO_x conversion, the CO conversion is an increasing function of d_r and T_{feed} (Fig. 6c). The X_{CO} dependence on d_r reflects that a leaner rich phase benefits the oxidation of CO by gas phase O_2 or stored

oxygen, as expected. The dependence on T_{feed} simply reflects that an increased temperature increases the rate of oxidation. Fig. 6d shows that NH_3 selectivity is a non-monotonic function of d_r . This trend reflects the similar trend for NO_x conversion versus d_r , although the

Table 2

Rich feed description for each of the five duty cycle rich (d_r) experiment feeds. For all other parameters: $\tau_i = 40$ s, $Q_T = 3000$ scfm; Lean feed constant across all experiments: 500 ppm NO, 1% CO, 3300 ppm H₂, 7% H₂O, 10% CO₂, 0.85% O₂; Rich feed: 500 ppm NO, 7% H₂O, 10% CO₂, Varied O₂, Varied CO/H₂ in a 3:1 ratio (total volume either 20 or 10 cc).

Feed	% O ₂	T _{feed} (°C)	V _{CO+H₂} (cc)	d_r ($S_{N,r} = 1$)
I	0.0	270	20	–
II	0.27	270	20	63%
III	0.27	470	20	63%
IV	0.53	270	20	47%
V	0.53	270	10	30%

maximum S_{NH_3} occurs at a lower d_r value than the d_r value resulting in a maximum in NO_x conversion.

The trends in the NH₃ production reflect the balance between NH₃ generation and consumption. A shorter and more intense rich phase is less effective in generating NH₃ as is a rich phase that is not sufficiently rich. At first glance, it may seem counterintuitive that NH₃ selectivity decreases as S_N decreases, as it was shown for steady state conditions that a rich environment leads to a higher NH₃ production (Fig. 2). However, the pulses for lower d_r are very short and concentrated which likely leads to a transient poisoning effect of CO on the Pt sites, which inhibits NO reduction to NH₃. As the rich phase becomes leaner (d_r and $S_{N,r}$ increasing) the selectivity and conversion increase to a maximum value before starting to decrease when the $S_{N,r}$ value approaches unity. The prolonged rich phase is insufficiently rich, which decreases the NH₃ generation rate and increases its oxidation rate. It is interesting to note that Feeds II–V follow the same locus of S_{NH_3} versus d_r for decreasing d_r . This trend suggests a limit on the NH₃ production when the rich phase is sufficiently rich. Indeed, the Feed I results clearly show that a critical variable in these experiments is the O₂ concentration. A rich phase devoid of O₂ gives the highest NH₃ yield over a wide range of rich duty fractions.

3.3.3. Impact of feed temperature

The data in Fig. 6 include two sets at identical conditions but two different feed temperatures of 270 and 470 °C, Feeds II and III, respectively. Similar qualitative trends for conversion and selectivity are evident up to a 60% rich duty ($S_{N,r} < 1$), but the magnitudes vary. At 470 °C the NO_x conversion is lower than it is at 270 °C while the NH₃ selectivity is considerably higher, or equivalently, the N₂ selectivity is much lower (given the relatively negligible N₂O selectivity). Note however that NH₃ yield (Fig. 6e) is nearly identical regardless of temperature, indicating the amount of NH₃ produced is not affected by temperature under these conditions. By definition, the variation in selectivity is due to the variation in NO_x conversion. The NO conversion trend is due in part to the decreased NO_x storage at higher temperatures with a larger fraction coming from direct catalytic conversion during the lean and rich phases. Recall that the steady state data show the NO conversion decreasing over this temperature range for a near-stoichiometric feed (Fig. 3a). On the other hand, the steady-state N₂ selectivity increases with temperature (Fig. 3b). This would appear to contradict the observed opposite trend during cyclic operation (Fig. 6d). Under steady-state conditions the increased N₂ selectivity is a result of the increased rates of NO bond scission and N adatom recombination. The high NH₃ selectivity achieved under cyclic conditions at 470 °C occurs at lower NO_x conversion and during the rich phase.

In order to better understand the effect of feed temperature on catalyst performance, Fig. 7 shows the NO_x, N₂O, NH₃, and CO effluent concentrations for feed temperatures of 270 °C and 470 °C and a 50% rich duty (lean and rich durations of 40 s). The NO_x transient data demonstrate that at lower temperatures there is a higher storage of NO_x, consistent with the NO_x storage data reported in Fig. 4. This observation explains why there is a higher NO_x conversion at the lower

temperature. Upon comparing the two profiles, both breakthroughs occur at the same time, although the lower temperature NO_x profile has a slower approach to saturation than at 470 °C. At higher temperatures the stored NO_x is not as stable and will undergo desorption and reduction. As shown in Fig. 4, we see that the storage exhibits two maxima, one around 175 °C and one around 300 °C, suggesting that the lean NO_x storage performance of the catalyst is sensitive the inlet temperature. At 470 °C, the TWNSC is less effective at storing NO_x under the conditions presented in this paper, but a higher frequency of lean-rich switching (i.e. shorter τ_i) would improve the performance. The individual NO and NO₂ profiles are shown in Fig. 7b. For these conditions, the extent of NO oxidation to NO₂ is dependent on the feed temperature, consistent with the lean NO_x conversion trends shown in Fig. 3. This behavior suggests that as the operating temperature changes, the cycling protocol can be adjusted to improve both NO_x conversion and storage efficiency. Additionally, at both feed temperatures the rich phase NO_x conversion is complete within 20 s of the rich phase feed, suggesting this portion of the cycle is independent of the temperatures used in this study.

The N₂O transient data show a moderate N₂O selectivity at 270 °C but a negligible level at 470 °C, consistent with typical N₂O behavior at low vs. high temperatures for NO_x storage catalysts. Unlike the results shown earlier for which a wider range of lean/rich switching (7.4 to 0.49) was employed and negligible N₂O was generated (Fig. 4), at 270 °C the narrow lean/rich switching of 1.24 to 0.60 results in a N₂O concentration as high as 50 ppm during the rich phase. The formation of N₂O during the rich phase only occurs during the first 20 s of the cycle, during which time stored O₂ is available. Once the oxygen storage is depleted, NO_x is fully reduced to N₂/NH₃.

The NH₃ transient data are nearly identical at the two feed temperatures. NH₃ breakthrough occurs about 10 s after the start of the rich phase, indicating the consumption of stored oxygen and NO_x occurring at similar rates in both cases. After breakthrough, the NH₃ concentration approaches 500 ppm, which indicates that NH₃ is the major product in this rich environment, independent of the temperature. NH₃ is not detected during the lean phase. The high selectivity at 270 °C is due to the increased storage of NO_x in the lean phase, and the yield is the same at both temperatures because the reactor environment is sufficiently rich to fully reduce NO_x to NH₃ instead of N₂, likely due to the high concentration of H₂ in the feed. While NH₃ decomposition is expected at higher temperatures, previous studies on similar catalyst compositions have shown that the presence of H₂ during regeneration can inhibit this phenomenon [33]. Additionally, there is a notable difference in the breakthrough profile depending on the temperature. At 270 °C, the NH₃ spikes much faster than at 470 °C, overshooting the feed NO value of 500 ppm, possibly due to the low CO breakthrough during this time as it is still oxidized by stored O₂. As the CO effluent concentration increases, the NH₃ production rate decreases due to the poisoning effect of CO on the reactive sites. However, at 470 °C, because the CO undergoes water gas shift, there is less poisoning and the NH₃ formation occurs more gradually, approaching 500 ppm as more H₂ is formed.

Finally, the CO transient data also reveal breakthrough at the same point as NH₃ upon oxygen depletion. While the 470 °C profile shows CO leveling off at about 700 ppm, the 270 °C profile shows a progressively increasing concentration during the rich phase. The differences can be attributed to a lower extent of CO conversion by reaction with H₂O at 270 °C than at 470 °C; i.e. the exothermic water gas shift reaction.

3.3.4. Impact of total cycle time

The total cycle time, τ_T , is another important operating parameter which must be tuned in conjunction with the rich duty fraction. We report in this section the impact of τ_T for several different cases corresponding to feeds of varying stoichiometric numbers, feed temperatures, and reductant types.

Fig. 8 shows the impact of total cycle time on catalyst performance

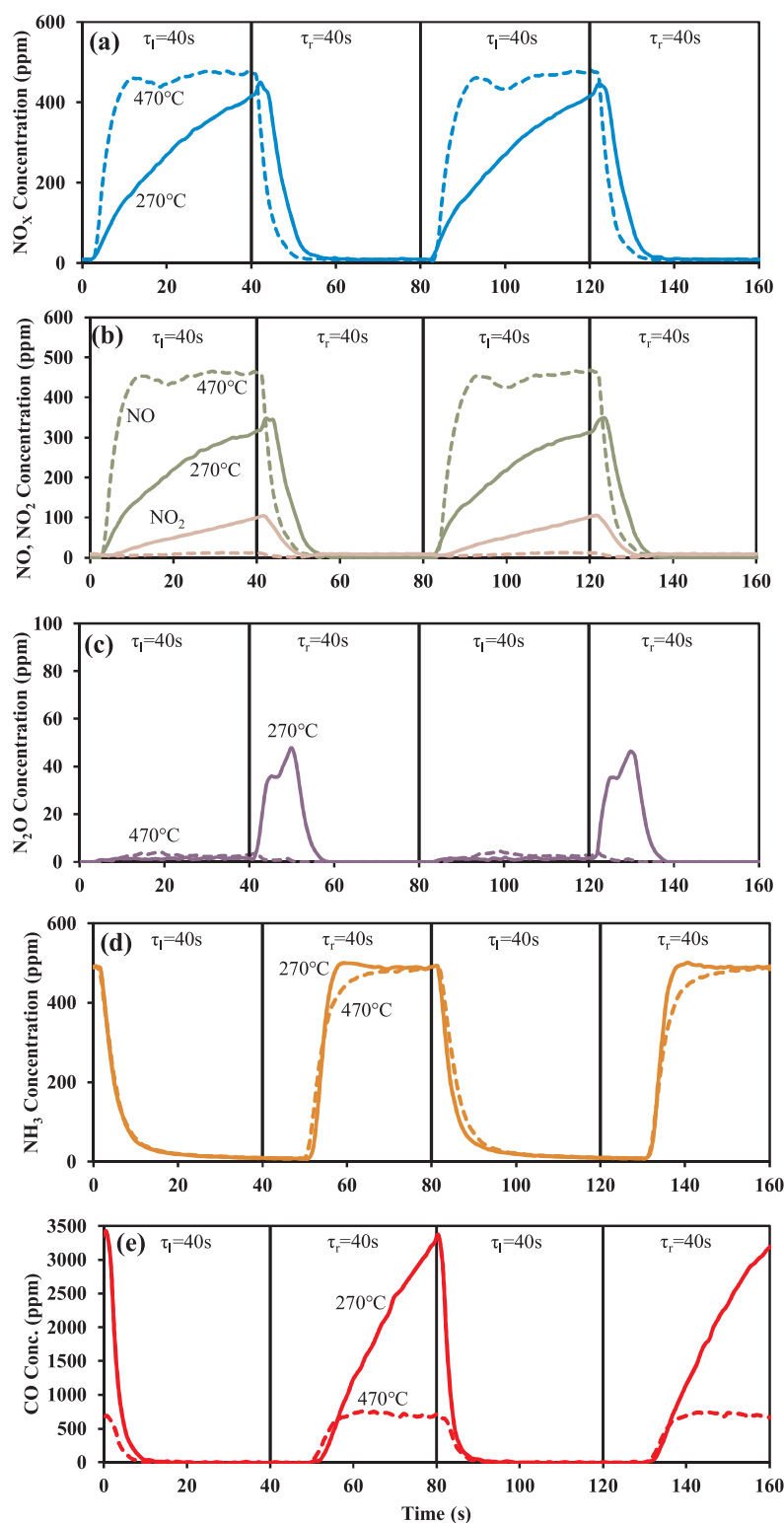


Fig. 7. a–e. Transient data for lean-rich cycling selected from d_r experiments at two feed temperatures and $d_r = 0.5$: 270 °C (—), 470 °C (---). (a) NO_x effluent concentration, (b) NO, NO_2 effluent concentration, (c) N_2O effluent concentration, (d) NH_3 effluent concentration, (e) CO effluent concentration. $\tau_l = 40$ s, $\tau_r = 40$ s. Lean inlet concentrations ($S_{N,l} = 1.24$): 500 ppm NO, 1% CO, 3300 ppm H_2 , 7% H_2O , 10% CO_2 , 0.8% O_2 . Rich inlet concentrations ($S_{N,r} = 0.60$): 500 ppm NO, 7% H_2O , 10% CO_2 , 0.27% O_2 , 0.75% CO, 0.25% H_2 .

for two different feed temperatures: 270 °C (Fig. 8a) and 470 °C (Fig. 8b) with a rich duty of 50%. This d_r value provides a relatively high NO_x conversion over this temperature range. The lean and rich O_2 concentrations are 5% and 0.37%, respectively, resulting in $S_{N,l}$ and $S_{N,r} = 7.4$ and 0.6, respectively. The ANR calculated using Eq. (7) is shown

on the secondary vertical axis.

With the wide disparity in lean and rich compositions a distinct NO_x conversion maximum is obtained for the 270 °C feed temperature (Fig. 8a). The maximum X_{NO_x} is 87% for a $\tau_T = 18$ s. At shorter cycle times the conversion falls off sharply, approaching 47% for $\tau_T = 4$ s. For

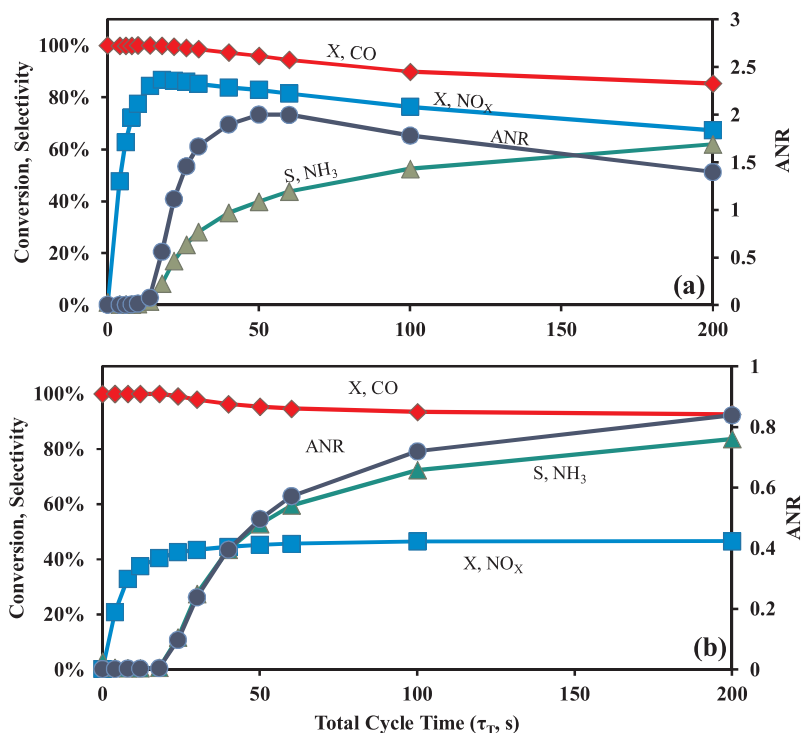


Fig. 8. a, b. Cycle-averaged conversion, selectivity and ANR for a Total Cycle Time experiment. $T_{\text{feed}} =$ (a) 270°C , (b) 470°C . DCR = 50%. Lean inlet concentrations ($S_{N,l} = 7.4$): 500 ppm NO, 1% CO, 3300 ppm H_2 , 7% H_2O , 10% CO_2 , 5% O_2 . Rich inlet concentrations ($S_{N,r} = 0.6$): 500 ppm NO, 1% CO, 3300 ppm H_2 , 7% H_2O , 10% CO_2 , 0.37% O_2 . (a) Peak NO_x conversion @ 20 s = 87%, ANR at 50 s (2.0). (b) Stable NO_x conversion @ 40 s, 44%.

longer cycle times the conversion decreases gradually, approaching 67% at $\tau_T = 200$ s. A NO_x conversion maximum at an intermediate cycle time was first reported by Kabin et al. [37], who examined a lean NO_x trap catalyst using propylene as the reductant. They showed that as the cycle time gets shorter, upstream mixing of the lean and rich feeds results in a feed approaching that of a “mixed feed” at steady state. For the current study, with rich and lean duties both 50%, the mixed feed would correspond to a simple arithmetic average of the two; i.e. O_2 feed concentration = $(5.0 + 0.37)\% / 2 = 2.69\%$ O_2 . Referring to earlier steady state results in Fig. 2, such a steady lean feed would result in a negligible NO_x conversion. Indeed, an extrapolation of X_{NO_x} to zero cycle time in Fig. 8a confirms this analysis. In contrast to the NO_x conversion, the CO conversion decreases monotonically with cycle time (Fig. 8a) from its maximum value of 100% for $\tau_T \rightarrow 0$, while the NH_3 selectivity monotonically increases from 0 starting at $\tau_T \sim 14$ s. The CO conversion decline merely reflects that with a more protracted rich phase, more reductant breaks through. In fact, the appearance of NH_3 at $\tau_T \sim 14$ s occurs at about the same point as the onset of the decrease in CO conversion, referring back to the transient profiles in Fig. 5a that show the coincident breakthrough of CO and NH_3 . The declining NO_x conversion combined with the increase in S_{NH_3} result in an ANR having a maximum at an intermediate cycle time; i.e. $\text{ANR} \sim 2.0$ at $\tau_T \sim 50$ s. As we expand on later, the existence of the NO_x conversion maximum and ANR maximum at two different cycle times poses an interesting operational question.

At 470°C neither the NO_x conversion nor the ANR exhibit maxima (Fig. 8b). Under these conditions the NO_x storage is much lower. As a result the catalyst performance is effectively a combination of lean and rich operations. The NO_x conversion increases sharply from the short cycle mixed-feed limit to ~47% at long cycle times. This value approaches the weighted average conversion of the lean feed (100%, $S_{N,r} = 0.6$) and rich feed (0%, $S_{N,l} = 7.4$) both operated at steady state. The NH_3 selectivity also increases monotonically from 0 at $\tau_T = 20$ s to 0.8 at $\tau_T = 200$ s. The magnitude of ANR is much lower at this rather high feed temperature.

For comparison, another cycle time sweep was carried out with a feed temperature of 270°C but a shorter rich duty of 14%. Fig. 9 shows the same performance metrics when the lean-rich switching is confined

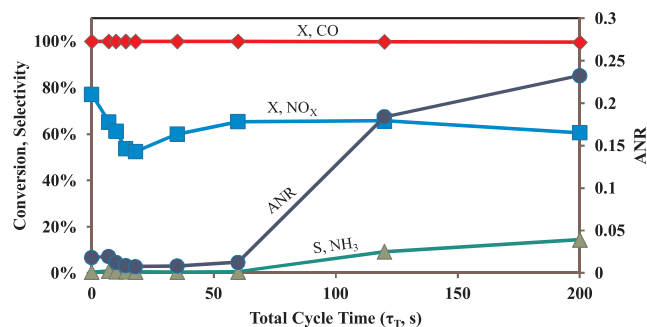


Fig. 9. Cycle-averaged conversion, selectivity and ANR for a Total Cycle Time experiment. $T_{\text{feed}} = 270^\circ\text{C}$. DCR = 14%. Lean inlet concentrations ($S_{N,l} = 1.18$): 500 ppm NO, 1% CO, 3300 ppm H_2 , 7% H_2O , 10% CO_2 , 0.8% O_2 . Rich inlet concentrations ($S_{N,r} = 0.83$): 500 ppm NO, 1% CO, 3300 ppm H_2 , 7% H_2O , 10% CO_2 , 0.53% O_2 .

to a S_N range between 1.18 (lean) and 0.83 (rich) and a feed temperature of 270°C . The NO_x conversion has two extrema over the τ_T range of 0–200 s total cycle time; a maximum of 77% for $\tau_T = 0$ s (obtained with a mixed feed and $S_N \sim 1.005$), and a minimum of 52% at $\tau_T = 18$ s. For the longest cycle time of $\tau_T = 200$ s, X_{NO_x} is ~61%. That the highest conversion is encountered with the continuously-fed mixed feed indicates that cycling is actually detrimental for this near-stoichiometric feed. The CO conversion exceeds 99% over the entire range of cycle times. NH_3 generation under these conditions is quite low with a maximum of only 14% selectivity achieved at a cycle time of 200 s while the net NH_3 generation is negligible for cycle times less than 60 s.

3.3.5. Impact of reductant type

Most of the experiments presented up to this point have involved a reductant feed containing CO and H_2 . In practice, the feed also contains hydrocarbons, so it is useful to assess the TWNSC performance when each of the three reductant types is present. Fig. 10 shows the results for a three-reductant feed (Fig. 10a) and a feed containing C_3H_6 as the sole reductant (Fig. 10b). Both experiments were conducted at the same feed temperature of 270°C while the rich duty was fixed at 50%. The C_3H_6

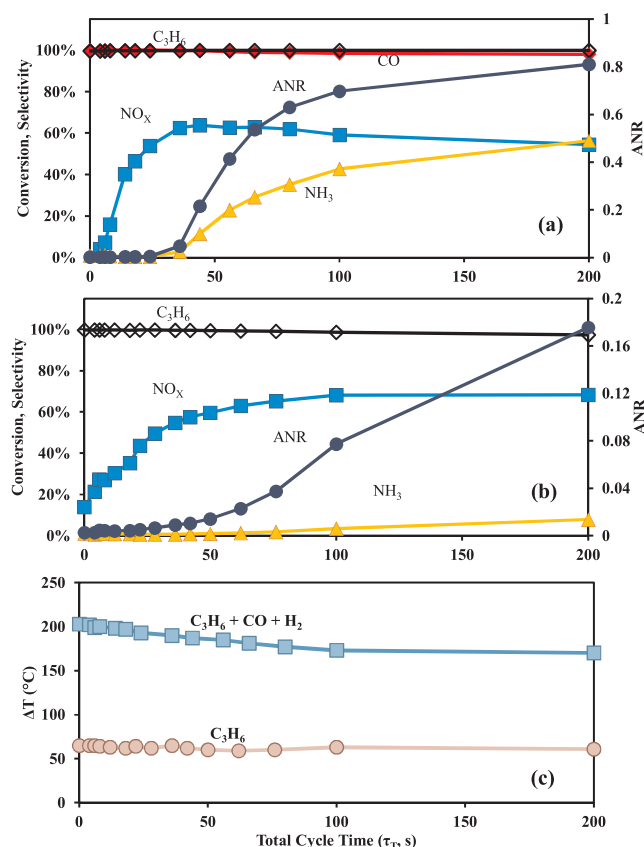


Fig. 10. a,b,c. (a,b) Cycle-averaged conversion, selectivity and ANR for a set of Total Cycle Time experiments. $T_{\text{feed}} = 270^\circ\text{C}$. DCR = 50%. Lean inlet concentrations ($S_{N,l} \sim 7.4$): a: 500 ppm NO, 1% CO, 3300 ppm H₂, 1000 C₃H₆, 7% H₂O, 10% CO₂, 8.4% O₂; b: 500 ppm NO, 1000 ppm C₃H₆, 7% H₂O, 10% CO₂, 3.4% O₂. Rich inlet concentrations ($S_{N,r} \sim 0.8$): a: 500 ppm NO, 1% CO, 3300 ppm H₂, 1000 ppm C₃H₆, 7% H₂O, 10% CO₂, 0.9% O₂; b: 500 ppm NO, 1000 ppm C₃H₆, 7% H₂O, 10% CO₂, 0.35% O₂. (a) Peak NO_x conversion @ 44 s = 64%. (c) Cycle averaged catalyst temperature rise (ΔT) for case a (C₃H₆ + CO + H₂) and b (C₃H₆).

Table 3

Concentration of reductants and O₂ during the lean and rich phase used in the reductant analysis cycling experiments explained in Fig. 11. In the cells labeled “Lean/Rich,” the corresponding concentration was used in both lean and rich phases.

	Set:	CO	H ₂	C ₃ H ₆	CO + H ₂	CO + H ₂ + C ₃ H ₆
O ₂	Lean	5%	5%	5%	5%	8.4%
	Rich	0.53%	0.53%	0.53%	0.53%	0.9%
CO	Lean/Rich	1.33%	–	–	1%	1%
H ₂	Lean/Rich	–	1.33%	–	0.33%	0.33%
C ₃ H ₆	Lean/Rich	–	–	0.147%	–	0.1%

concentration in the lean and rich phases for each experiment was fixed at 1000 ppm while the CO and H₂ concentrations were 1% and 3300 ppm, respectively, for the three-reductant feed. The O₂ concentrations in the rich and lean phases were adjusted to ensure that the $S_{N,r}$ and $S_{N,l}$ were fixed at 7.4 and 0.8, respectively. Table 3 reports the feed concentrations. Note that the exothermic heat effects (Fig. 10c) are larger for the three-reductant feed.

For the three-reductant feed results (Fig. 10a) there is a distinct maximum in the NO_x conversion ($\sim 64\%$) at $\tau_T \sim 44$ s. At the cycle time limits of 4 s (mixed feed) and 200 s, NO_x conversion is ~ 0.2 and $\sim 56\%$, respectively. In contrast, for the C₃H₆ only feed (Fig. 10b) the NO_x conversion increases monotonically from $\sim 12\%$ at $\tau_T = 4$ s to $\sim 68\%$ at $\tau_T = 200$ s. The comparison shows that C₃H₆ is more effective

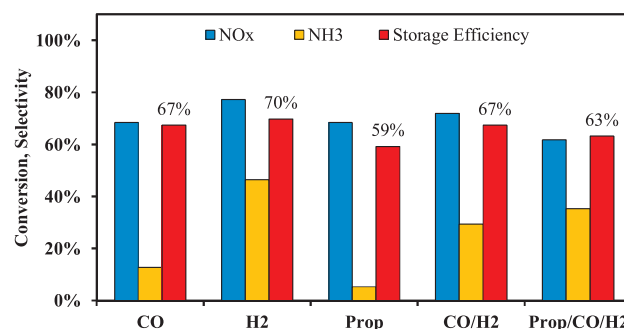


Fig. 11. NO_x conversion and NH₃ selectivity for various combinations of reductant in the feed. $T_{\text{feed}} = 270^\circ\text{C}$. Total cycle time, 80 s, $\tau_1 = 40$ s, $\tau_r = 40$ s. All feeds contained 10% CO₂, 7% H₂O, 500 ppm NO, and varying concentrations of CO, H₂, C₃H₆, and O₂ to achieve $S_{N,l} = 7.6$ and $S_{N,r} = 0.83$ (see Table 3).

in reducing NO_x than the three-component mixture for shorter cycle times ($\tau_T < \sim 10$ s) and nearly as effective for longer cycle times. The short cycle time difference may be due to CO inhibition as was discussed earlier (Figs. 2 and 3). Each case shows nearly complete conversion of the reductant over the entire range of cycle times. This is the result of the overall lean conditions ($S_N \sim (7.4 + 0.8)/2 = 4.1$). On the other hand, a large difference is evident in NH₃ generation under these conditions. Clearly CO and H₂ are much more effective in generating NH₃. Corresponding to these trends is a much higher ANR for the three-reductant feed than the propylene-only feed. This is not surprising given that NO conversion by H₂ to NH₃ is very effective under these conditions.

Fig. 11 shows the effect of using various combinations of reductants on the cycle-averaged NO_x conversion and NH₃ selectivity. To enable a meaningful comparison, the cycle time and rich duty ($\tau_T = 80$ s; $d_r = 0.5$), feed temperature (270 °C) and stoichiometric numbers for both the lean ($S_{N,l} = 7.6$) and rich phases ($S_{N,r} = 0.83$) were fixed. Species concentrations were adjusted to maintain the fixed $S_{N,l}$ and $S_{N,r}$ values. Overall, the conversion of NO_x varies less with the type of reductant in the feed than does the NH₃ selectivity. X_{NO_x} varies between 62% (mixture of three reductants) and 77% (H₂ only) while S_{NH_3} varies between 45% (H₂ only) and 5% (C₃H₆). In maximizing both NO_x conversion and NH₃ selectivity, H₂ is the most effective reductant [26,30]. Any feed that contains H₂ increased the NH₃ selectivity, consistent with the discussion in previous sections regarding the enhancement of H₂ on NH₃ selectivity.

To better understand these trends, Fig. 12a shows the transient effluent NO_x concentration for one lean-rich cycle using each of the reductant feeds. Each of the NO_x profiles are qualitatively similar, i.e., during the lean phase there is a brief period of complete NO_x trapping followed by NO_x breakthrough with a gradual increase; during the rich phase there is a NO_x spike followed by a sharp decrease. Overall the data show that H₂ is the most effective reductant, followed by CO/H₂. The NO_x conversion is primarily affected by two factors, the lean storage and the intensity of the NO_x spike that occurs during the lean-rich transition. An estimate of the lean NO_x storage efficiency (η_l), determined using Eq. (8), is highest for H₂ (70%) and lowest for propylene (59%). The C₃H₆ data shows the steepest NO_x breakthrough during the first half of the lean phase while all of the other feeds have nearly identical NO_x breakthroughs during this period. Interestingly, the C₃H₆-only NO_x breakthrough intersects the three-component feed near the end of the lean period. The NO_x concentration during the rich phase shows greater disparity in the several cases. For feeds containing CO, the NO_x spike is most pronounced. This would appear to indicate that CO inhibits the regeneration. The comparison of the CO-only and H₂-only or the propylene-only and the three component feeds underscore this point.

Fig. 12b shows the corresponding transient mid-point catalyst

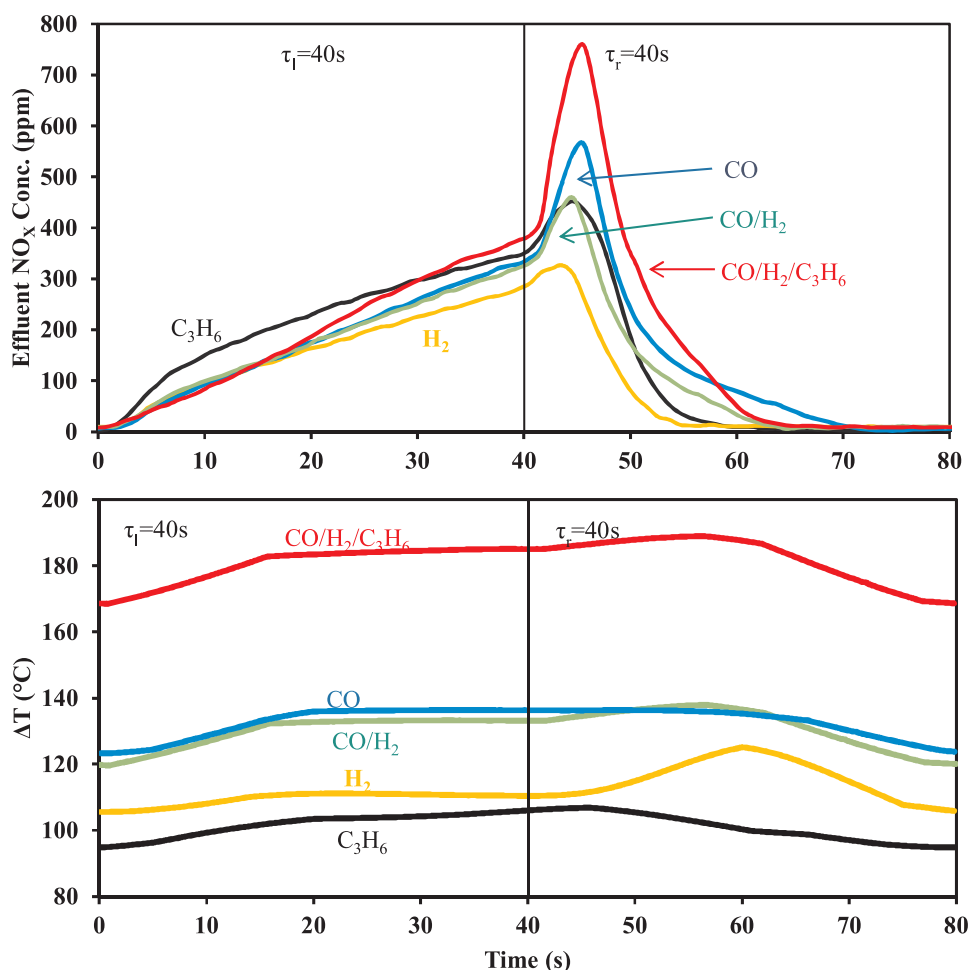


Fig. 12. a,b. (a) Transient NO_x concentration profile for one lean/rich cycle for various combinations of reductants, taken from raw data of experiments described in Fig. 10. (b) Temperature rise of one cycle for each of the five feeds described in Fig. 10. $\tau_l = 40$ s, $\tau_r = 40$ s, $T_{\text{feed}} = 270$ °C, $S_{N,l} = 7.6$, $S_{N,r} = 0.83$ (see Table 3).

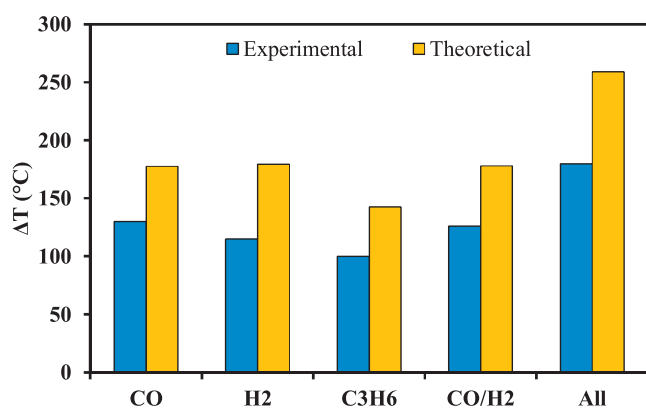


Fig. 13. Comparison of cycle-averaged catalyst temperature rise to theoretical values calculated according to Eq. (10).

temperature. For all feeds, there is a gradual increase during the lean phase (oxidation), followed by a decrease during the rich phase (reduction). The lowest temperature rise is encountered with the propylene-only case, followed by the H₂ case, and then the CO containing cases. The highest temperature rise is seen with the three-reductant feed. Fig. 13 shows the measured, cycle-averaged temperature rise for each case compared to an estimate for the theoretical steady-state value using the following expression for the adiabatic temperature rise:

$$\Delta T = \frac{-\Delta H_{\text{rxn}} X C_r}{C_p} \quad (10)$$

where ΔH_{rxn} is the heat of combustion of the reductant, X is the conversion, C_r is the concentration (volume percentage), and C_p is the heat capacity of the feed gas. As shown in the figure, there is agreement in the trend between the temperature rise of individual species and the reductant mixtures. However, there is an overall difference in magnitude between the measured and theoretical values, most attributed to reactor heat losses. The observed conversion of each reductant mixture in this set of experiments is more than 98%. As such, the temperature rise values are attributed to variations in reductant concentration and the heat of combustion of each species.

3.4. Optimal operation

The TWNSC performance results suggest that system optimization is nontrivial. The manipulated operating parameters include the cycle time, rich duty fraction, rich phase O₂ concentration, and feed temperature. The choice of which performance metric is the most critical depends on intended application of the TWNSC. For the standalone TWNSC, operating conditions should be selected that maximize the NO_x conversion, reductant conversion, and N₂ selectivity while minimizing the reductant usage. In contrast, for the TWNSC followed by a SCR, the NO_x conversion should be balanced across both reactors to take advantage of the lower cost SCR. In that case the rich phase operating conditions should be selected that give a NO_x conversion approaching 50% and a NH₃ selectivity as high as possible to impact

downstream SCR, i.e. ANR ~ 1 [20,21]. Identifying the precise operating conditions would require a detailed multi-variable optimization.

To illustrate the optimization strategy, it is instructive to evaluate the case when cycling is done with widely different feed compositions. Fig. 8a shows such a case using CO + H₂ as the reductant mixture that might represent a lean gasoline application. In those experiments the data reveal the existence of two maxima obtained at different cycle time values. The first maximum is of the NO_x conversion while the second is of the ANR. Selecting the NO_x conversion maximum (87%) as the operating point for the standalone TWNSC would require a total cycle time of ~ 18 s at the duty rich fraction of 50%. Under these conditions the NH₃ selectivity is rather low ($\sim 20\%$) and the CO conversion is very high ($\sim 99.9\%$). On the other hand, for the TWNSC + SCR configuration, there are two potential operating points at which ANR ~ 1 . If a downstream SCR catalyst is available, as mentioned earlier the optimal ANR value is unity. The first is to the left of the ANR maximum, while the second is well to the right of the ANR maximum (e.g., at $\tau_T \sim 20$ s and at $\tau_T \sim 200$ s, respectively). The latter would appear to be the better choice as $X_{\text{NO}_x} \sim 67\%$ and $S_{\text{NH}_3} \sim 62\%$ which are closer to the desired optimal values of 50% and 100%, respectively. However, the CO conversion at this cycle time is 85%, an issue that still needs to be addressed for a TWNSC system. Another potential operating point might be at the ANR maximum which occurs for $\tau_T \sim 50$ s. In this case the NO_x conversion is $\sim 83\%$ and the NH₃ selectivity is $\sim 44\%$. Moreover, the CO conversion is 96%. Obviously, this illustration oversimplifies the optimization but it does provide insight into the main issues.

The catalyst performance is qualitatively different at a higher feed temperature (Fig. 8b). Because the lean NO_x storage is poor at 470 °C, the cycle-averaged conversion stabilizes after only 40 s instead of exhibiting a maximum, indicating that even with longer lean periods, the NO_x breaks through and increases to its feed concentration within 40 s. Another key difference at the higher feed temperature is that the NH₃ selectivity and ANR steadily increase. The ANR value does not approach 1.0 in these conditions, mostly due to the decrease in NO_x conversion at higher feed temperature. Since the NO_x conversion stabilizes, we would expect NH₃ selectivity to increase because a longer rich period generates more NH₃. To optimize this system, a total cycle time of 40 s would be a good choice leading to 45% NO_x conversion and a reasonable NH₃ selectivity (ANR of 0.4, and a CO conversion of 96%). A higher cycle time would lead to better NH₃ yield, but long cycle times are much less practical for engine operation, and the additional loss of CO conversion is problematic.

4. Conclusions

A systematic study of the performance of a commercial three-way NO_x storage catalyst (TWNSC) was conducted. The study provides insight about the potential for its use in lean-burn gasoline vehicle exhaust as a standalone unit or the first of two units in tandem with a downstream SCR. The steady-state performance expectedly shows the demarcation between rich and lean such that within a narrow window around the stoichiometric neutral point high conversion of CO, hydrocarbon (C₃H₆), and NO can be achieved. In general, CO and C₃H₆ conversions increase with temperature and stoichiometric number S_N , while NO_x conversion and NH₃ production decrease with increasing temperature and S_N .

The performance features under lean/rich cycling are amenable for either standalone TWNSC or the tandem TWNSC + SCR configuration. The cycling protocol may be designed to achieve a high NO_x conversion and N₂ selectivity, but this will generally require reductant exceeding a threshold value that leads to difficulty in avoiding NH₃ and CO slip whereas insufficient reductant will lead to an inadequate NO_x conversion. The concentrations of reductant and O₂, duration of the rich pulse (duty fraction), and cycle time may be tuned to achieve a desired NO_x conversion and/or NH₃ selectivity. If there is a large disparity in the lean/rich ratio over the cycle, the NO_x conversion exhibits a maximum

value at an intermediate cycle time, as does the ammonia to NO_x ratio. Optimization should be possible for a particular application that maximizes the NO_x conversion and reductant utilization. Clearly, the optimization would benefit from modeling, which will be discussed in a forthcoming companion publication.

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